

Pressure-Induced Phase Transition of $C_{12}E_5$ Micelles

Nonionic surfactants form a variety of microstructures in water, ranging from simple micelles at low surfactant concentrations to complex mesophases, such as hexagonal or lamellar phases at high concentrations. The effect of pressure on the structure of micelles and microemulsions has not been extensively studied. Small angle neutron scattering (SANS) is particularly well suited for such measurements because the range of length scales probed includes both the particle size and the interparticle spacing.

Pressure effects observed in SANS measurements of surfactant microstructure are typically interpreted in terms of geometric packing arguments that focus on the compressible hydrophobic tails of the surfactants. In this context, increasing pressure has the single effect of decreasing the surfactant tail volume, thereby increasing the curvature of the oil-water interface. Conversely, increasing temperature dehydrates the nonionic headgroups, decreasing the headgroup area and decreasing the film curvature. Thus, temperature and pressure can be viewed as thermodynamic variables with inherently different mechanisms and opposite effects for controlling microstructure in nonionic surfactant solutions.

Here we report the results of high-pressure SANS experiments at 20 °C and pressures up to ≈ 300 MPa on a solution of pentaethylene glycol mono-n-dodecyl ether ($C_{12}E_5$) in D_2O having a mass fraction of 1 %. The phase diagram for this system [1] at ambient pressure is shown in Fig. 1. At this temperature and surfactant concentration, a single-phase micellar solution (L_1 phase) forms at ambient pressure, well below the lower critical solution temperature (LCST) for liquid-liquid equilibrium and far removed from the H_1 hexagonal phase at much higher $C_{12}E_5$ concentrations. The microstructure of the L_1 -phase at ambient pressure is known to be a network of branched semi-flexible, cylindrical micelles with the branch points comprised of three-armed junctions.

SANS spectra were measured using the NIST high-pressure cell and neutrons of wavelength $\lambda = 6$ Å, covering a q -range of $0.012 \text{ Å}^{-1} < q < 0.22 \text{ Å}^{-1}$. The scattering curves obtained at 3.4 MPa, 241 MPa, and 255 MPa are shown in Fig. 2. The curves at 3.4 MPa and 241 MPa are virtually identical, indicating no significant change in microstructure with increasing pressure up to 241 MPa. Fitting these curves

using a form factor for cylindrical micelles gives a radius of $(21.0 \pm 0.2) \text{ Å}$ and a length greater than 600 Å, independent of pressure. However, a small increase in pressure from 241 MPa to 255 MPa leads to the appearance of a peak in the scattering intensity at $q \approx 0.130 \text{ Å}^{-1}$, indicative of a locally ordered system. A similar transition has been reported in high-pressure SANS studies of tetradecyldimethylaminoxide (TDMAO) micelles in D_2O at pressures up to 300 MPa, but the high-pressure microstructure was never determined [2].

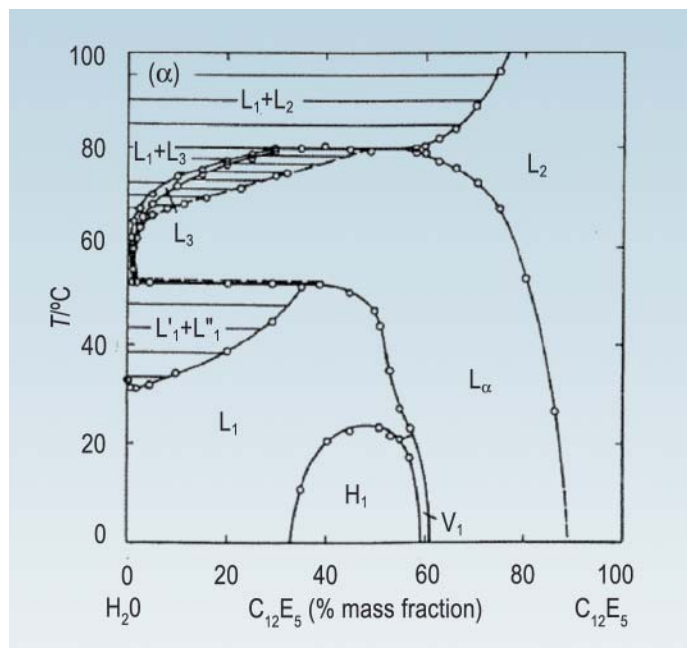


FIGURE 1. Temperature-composition phase diagram for $C_{12}E_5$ /water solutions at ambient pressures [1].

Shown in Fig. 2 is the scattering curve for the H_1 hexagonal phase at 49 % $C_{12}E_5$ mass fraction at 20 °C, and ambient pressure. The peak at $q \approx 0.120 \text{ Å}^{-1}$, arising from the hexagonal lattice of cylindrical micelles, is similar to the peak for the 1 % $C_{12}E_5$ mass fraction solution at 255 MPa, suggesting that this new high-pressure phase may resemble a slightly compressed state of the H_1 hexagonal phase at ambient pressure. The formation of a lamellar phase from cylindrical micelles is unlikely, since this corresponds to increasing the hydrophobic core volume-to-surface-area ratio per surfactant molecule, or equivalently, decreasing the spontaneous curvature of the surfactant film. The application

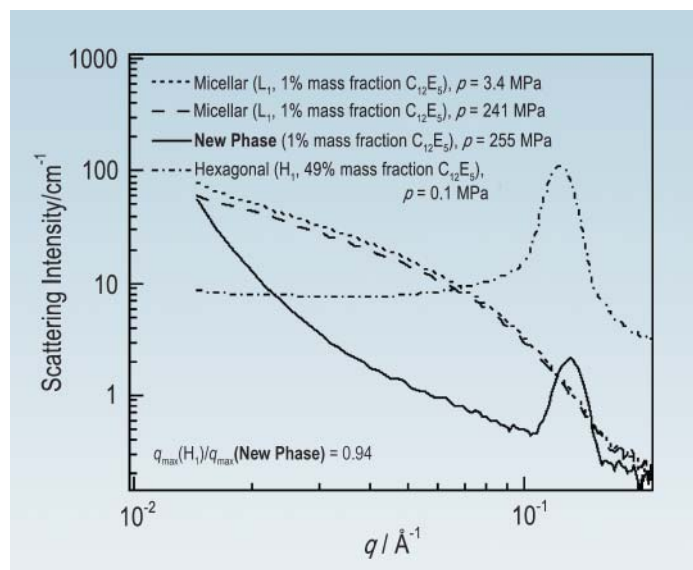


FIGURE 2. Measured SANS spectra at 20 °C for 1 % mass fraction $C_{12}E_5$ in D_2O as a function of pressure and 49 % mass fraction $C_{12}E_5$ in D_2O at ambient pressure.

of pressure would have the opposite effect. We conclude, therefore, that the observed change in microstructure corresponds to a pressure-induced L_1 - H_1 phase transition from a network of branched semi-flexible, cylindrical micelles to hexagonally ordered bundles of cylindrical micelles.

To further understand the SANS results, we have measured the temperature dependence of the L_1 - H_1 transition pressure and find that the p - T curve follows the p - T freezing curves for liquid n -alkanes of comparable hydrocarbon chain length. N -decane solidifies at a pressure of ≈ 250 MPa at 20 °C, which is close to the pressure for the observed L_1 - H_1 phase transition. We propose that the $C_{12}E_5$ micelle hydrophobic core, equivalent to n -decane, does solidify at these conditions, such that the micelles lose flexibility, and hence conformational entropy. An analysis of the geometric packing constraints for three-arm junctions coexisting with cylinders shows that when the surfactant tail volume decreases with increasing pressure, the fraction of surfactant forming junction points also decreases. This indicates that the formation of three-arm junctions becomes increasingly unfavorable at higher pressures due to the compression of the $C_{12}E_5$ micelle hydrophobic core. Our calculations predict that no junctions should be present at $P > 275$ MPa at 20 °C,

which is in good agreement with our observation of a structural transition between 241 MPa and 255 MPa at this temperature. Consequently, the network of branched thread-like micelles becomes globally unstable. The formation of hexagonally ordered bundles of cylindrical micelles follows as the attractive van der Waals forces between the micelles are not offset by entropic repulsive undulation interactions that are not present in the now-solidified hydrophobic core.

The practical significance of these results is to show that pressure allows access to regions of the $C_{12}E_5$ /water phase diagram that are virtually inaccessible to temperature. Thus, the use of pressure may offer unique approaches for directing and stabilizing certain surfactant microstructures that, in turn, could prove useful for creating novel soft materials.

References

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- [2] N. Gorski, J. Kalus, D. Schwahn, Langmuir **15**, 8080 (1999).